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(54) Titre : PROCÉDE EN UNE OU PLUSIEURS ETAPES POUR LA PREPARATION DE DISPERSIONS DE  
POLYMERES HYDROSOLUBLES A FAIBLE VISCOSITE

(54) Title: SINGLE-STAGE OR MULTI-STAGE PROCESS FOR MAKING LOW-VISCOSITY, WATER-SOLUBLE  
POLYMER DISPERSIONS

(57) Abrégé/Abstract:

Low-viscosity, water-soluble polymeric aqueous dispersions with high active substance concentrations containing a polymer (A), made up of water-soluble monomers (a1) and, optionally, amphoteric monomers (a2), as well as a polymeric dispersion agent (D) may be prepared by removing water during the polymerization of the polymer (A), in the presence of the polymeric dispersion agent (D) to afford the polymeric dispersion (PD'). In another embodiment, the process involves the addition of the polymeric dispersion agent (D) in aqueous solution to the polymeric dispersion (PD') in a second process stage, which leads to the polymeric dispersion (PD'').



ABSTRACT OF THE DISCLOSURE

Low-viscosity, water-soluble polymeric aqueous dispersions with high active substance concentrations containing a polymer (A), made up of water-soluble monomers (a1) and, optionally, amphoteric monomers (a2), as well as a polymeric dispersion agent (D) may be prepared by removing water during the polymerization of the polymer (A), in the presence of the polymeric dispersion agent (D) to afford the polymeric dispersion (PD'). In another embodiment, the process involves the addition of the polymeric dispersion agent (D) in aqueous solution to the polymeric dispersion (PD') in a second process stage, which leads to the polymeric dispersion (PD").

TITLE OF THE INVENTION

SINGLE-STAGE OR MULTI-STAGE  
PROCESS OR MAKING LOW-VISCOSITY,  
WATER-SOLUBLE POLYMER DISPERSIONS

5

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a single-stage or multi-stage process for making low-viscosity, water-soluble polymer dispersions containing at least one polymeric  
10 dispersion agent (D) and one polymer (A), said polymer comprising (a1) at least one water-soluble monomer and, optionally, (a2) at least one amphoteric monomer.

Discussion of the Background:

15

Aqueous dispersions of water-soluble polymers are used, for example, as flocculents during waste water treatment, as dehydration agents after separation of the aqueous phase, as retention agents after separation of the aqueous phase, as retention agents in paper-making, as soil  
20 improvement agents, or as dispersion agents.

EP 170 394 describes a liquid that can be mixed with water and that consists of particles, built up of a high-molecular weight polymer and having particle sizes of more than 20  $\mu\text{m}$ , in an aqueous solutions as the continuous phase  
25 that contains an equilibration agent that maintains the balance between the water content of the gel particles and

the water content in the continuous phase and which thus prevents agglomeration of the gel particles. As preferred equilibration agents, one uses the sodium salt of polyacrylic acid or poly(diallyldimethylammonium chloride) 5 (Poly-DADMAC).

EP 183 466 describes a process for making a water-soluble polymer dispersion, characterized by polymerizing a water-soluble monomer while stirring in an aqueous solution of at least one salt in the presence of a 10 dispersion agent. In this process, one uses polyols, poly(alkylene ethers), alkali salts of poly(acrylic acid), as well as alkali salts of poly(2-acrylamido-2-methylpropanesulfonic acid) as dispersion agents.

DE-PS 29 24 663 discloses a process for making an 15 aqueous dispersion from a water-soluble polymer with good stability and flowability, where the water-soluble polymer contains at least one water-soluble ethylenically unsaturated monomer and where poly(alkylene ether), polyethyleneimine and other polymers may be present as 20 dispersion agents. The aqueous dispersions thus made can -- possibly after dilution with water -- be used as flocculation aids, as thickening agents, as soil conditioning agents, and for other uses.

DE 43 16 200 A1 describes aqueous dispersions of 25 water-soluble polymers, formed by polymerization of a mixture, consisting of water-soluble, hydrophobic, and, optionally, amphoteric monomers in the presence of a polymeric dispersion agent. A two-stage process for making low-viscosity aqueous dispersions of water-soluble

polymers, according to DE 42 16 167 A1, with an increased content of active substance, is covered by DE 43 16 200 A1. DE 43 35 567 A1 describes an at least three-stage process for making low-viscosity aqueous dispersions of water-soluble polymers, which means that the content of active substance can be increased even further. In these processes, the aqueous polymer dispersion is made, in a first stage, according to DE 42 16 167 A1, in a second stage the content of active substance in the polymer dispersion is increased by removing water, and in a third stage, additional quantities of polymeric dispersion agent are added, while the second and third process stages can be repeated successively thereafter.

EP-A 262 945 describes homogeneous mixtures of two water-soluble polymers, with one polymer being made in the aqueous solution of the other polymer by polymerization of the water-soluble monomers. The polymer, present in the solution, preferably has an average molecular weight of less than  $10^6$  Daltons while the polymer, polymerized in the aqueous solution, has a molecular weight of at least  $2 \times 10^6$  Daltons.

The aqueous solutions, described in EP 170 394 and containing gel particles, suffer from the disadvantage that they exhibit highly increased viscosities after standing for a long time; these viscosities can be reduced only by using shear rates, such as, for example, intensive stirring. The rheological properties here depend on a complex balance between polymer, equilibration agent, water content, and particle size of the gel particles.

EP 183 466 describes water-soluble polymers as dispersions in aqueous salt solutions, with the help of a dispersion agent. A disadvantage of these dispersions is the high salt content of the aqueous phase (up to 30% by weight), as compared to a relatively small polymer (active substance) content (of up to 20% by weight) that leads to waste water problems when such dispersions are used for certain purposes.

The large amounts of dispersion agent -- in relation to the water-soluble polymer -- often have a prohibitive effect with regard to the use of the aqueous dispersions according to DE-PS 29 24 663. If one uses such dispersions, for example as flocculents for electrically charged particles, then the effect of the high-molecular weight ionic polymers is reduced by the dispersion agent that has a lower-molecular weight in comparison.

Thus, inspection of the state of the art reveals that there exists the problem of making available aqueous

dispersions of water-soluble polymers that have a low viscosity, a high content of an active polymer substance having a high molecular weight, as well as a salt-free water phase. This problem is solved by the polymer aqueous  
5 dispersions described in DE 42 16 167 A1. Moreover, DE 43 16 200 A1 or DE 43 35 567 A1 provide two-stage or a multi-stage processes according to which the low viscosity or high content of high molecular weight polymer -- as obtained in DE 42 16 167 A1 -- can be further reduced  
10 (viscosity) or increased (active substance content and/or molecular weight).

As noted above, EP-A 262 945 describes homogeneous mixtures of two water-soluble polymers that are made by forming a polymer in the aqueous solution of the other  
15 polymer, with one polymer being selected from the group of polycations, preferably, with molecular weights of less than  $10^6$  Daltons. The active substance concentrations achieved in EP-A 262 945 amount to a maximum of between 30 and 35% by weight based on the weight of the aqueous  
20 dispersions.

The solutions proposed -- especially in DE 42 16 167 A1, DE 43 16 200 A1, and DE 43 35 567 A1, as well as in EP-A 262 945 -- were intended to provide aqueous dispersions of water-soluble polymers that have  
25 a low viscosity along with a high content of active

polymer substance and an absence of additional auxiliary substances in the water phase. In spite of these solutions, there still remains a need for increasing the amount of active polymer agent in the aqueous phase, especially in the case of active polymer substances that contain large portions of water-soluble monomers that, for example, during the dilution of the dispersion, develop a thickening effect, along with small amounts of hydrophobic monomers, that, in turn, do not develop any such thickening effect.

#### SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide novel methods for preparing low-viscosity, water-soluble polymer aqueous dispersions.

15 It is another object of the present invention to provide methods for preparing low-viscosity, water-soluble polymer aqueous dispersions which contain high concentrations of the polymer.

20 It is another object of the present invention to provide low-viscosity, water-soluble polymer aqueous dispersions which are useful as flocculation agents for electrically charged suspended particles.

It is another object of the present invention to provide low-viscosity, water-soluble polymer aqueous



dispersions which are useful as retention agents in paper making.

It is another object of the present invention to provide low-viscosity, water-soluble polymer aqueous  
5 dispersions which are useful as thickening agents.

It is another object of the present invention to provide low-viscosity, water-soluble polymer aqueous dispersions which are useful as dehydration agents.

It is another object of the present invention to  
10 provide low-viscosity, water-soluble polymer aqueous dispersions which are useful as soil improvement agents.

These and other objects, which will become apparent during the following detailed description, have been achieved by the inventors' discovery that highly-  
15 concentrated, low-viscosity, water-soluble polymer aqueous dispersions (PD' or PD'') that contain at least one polymeric dispersion agent (D), as well as one polymer (A), said polymer (A) being prepared by polymerizing a monomer mixture comprising:

- 20 (a1) 80 to 100% by weight, preferably 80 to 99% by weight, more preferably 85 to 95% by weight, based on the total weight of the monomer mixture, of at least one water-soluble monomer; and, optionally,
- 25 (a2) 0 to 20% by weight, preferably 1 to 20% by weight, more preferably 5 to 15% by weight, based

on the total weight of the monomer mixture, of at least one amphoteric monomer,

wherein the sum of amounts of monomer (a1) and monomer (a2) is 100% by weight, and wherein the polymer (A) has a weight average molecular weight,  $M_w$ , of at least  $10^6$  Daltons and wherein the polymeric dispersion agent (D) is preferably a polyelectrolyte with a weight average molecular weight,  $M_w$ , of less than  $5 \times 10^5$  Daltons or a poly(alkylene ether), such as a poly(alkylene ether) with alkylene groups having 2 to 6 carbon atoms, and wherein (D) is incompatible with (A);

may be prepared by carrying out the polymerization of monomer (a1) and, optionally, monomer (a2) to obtain polymer (A) in an aqueous dispersion which comprises polymeric dispersion agent (D), and removing water from the aqueous dispersion during the polymerization.

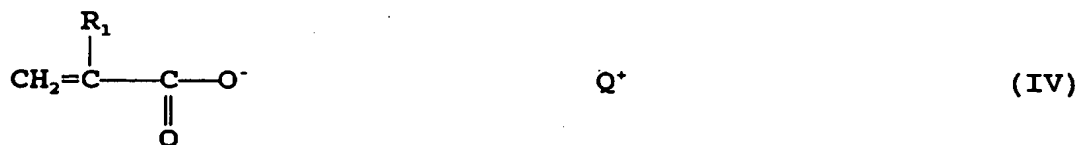
The present method may be carried out as a single-stage or multi-stage process. Thus, in the first stage, an aqueous dispersion (PD) of the water soluble polymer (A) is obtained by polymerizing monomers (a1) and, optionally (a2) in an aqueous medium containing at least one polymeric dispersion agent (D). During the polymerization, water is removed from the developing polymeric dispersion (PD), preferably by evaporation or distillation, for example, at normal pressure or with the application of a vacuum. This single-stage embodiment affords the polymeric dispersion (PD'). Thereafter, preferably in a second stage, an aqueous solution containing an additional amount of

polymeric dispersion agent (D) may be added to polymeric dispersion (PD') to obtain the polymeric dispersion (PD").

After completion of the second stage, one can once again remove water from the polymeric dispersion (PD"), thus formed, and one can once again add an additional portion of the aqueous solution containing the polymeric dispersion agent (D), in order to obtain an even higher active substance concentration. In accordance with the process of the present invention, it is possible to increase the active substance concentration of the (PD) polymeric dispersions that contain a water-soluble polymer (A) and dispersion agent (D), without causing the viscosity of the polymeric dispersions (PD') or (PD") to rise so high that the handling of polymeric dispersions, made in this fashion, is made comparatively more difficult by the resultant instability during shear stress.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a preferred version of the invention, at least one of the water soluble monomers (a1) has at least one ionic group. As (a1) monomers, one can employ, for example, salts of acrylic and/or methacrylic acid according to the general formula (IV):



wherein: R' is hydrogen or methyl; and  
 Q<sup>+</sup> is an alkali metal ion, such as, for example, Na<sup>+</sup> or K<sup>+</sup>; an ammonium ion, such as, for example, NH<sub>4</sub><sup>+</sup>, 'NR"<sub>2</sub>H<sub>2</sub>, 'NR"<sub>3</sub>H or 'NR"<sub>4</sub>, in which R" is alkyl with 1 to 6 carbon atoms; or another monovalent, positively charged ion.

The (a1) monomers according to formula (IV), for example, include sodium (meth)acrylate, potassium (meth)acrylate or ammonium (meth)acrylate. In the context of the present invention, it is to be understood that the terms "(meth)acrylate" and "(meth)acrylamide" refer to "methacrylate and/or acrylate" and "methacrylamide and/or acrylamide", respectively.

Furthermore, for example, one can use acrylic and/or methacrylic acid itself as the monomer (a1) component, as well as (meth)acrylamides according to formula (V):



wherein:  $R^{III}$  is hydrogen or methyl; and  
 $R^{IV}$  and  $R^V$ , independently of each other, are  
hydrogen, alkyl with 1 to 5 carbon atoms, or  
hydroxyalkyl with 2 to 5 carbon atoms.

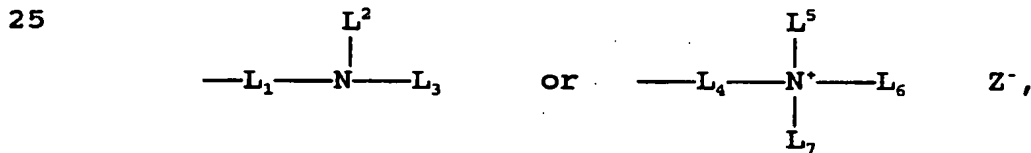
5 The following might be mentioned by way of example as  
(a1) monomers according to formula (V):

(meth)acrylamide, N-methyl(meth)acrylamide, N,N-  
dimethyl(meth)acrylamide, N,N-diethyl(meth)acrylamide, N-  
methyl-N-ethyl(meth)acrylamide as well as N-  
10 hydroxyethyl(meth)acrylamide. Such (meth)acrylamides can  
be prepared as described in Kirk-Othmer, Encyclopedia of  
Chemical Technology, vol. 15, pp. 346-376, 3rd. Ed., Wiley  
Interscience, 1981.

Furthermore, monomers according to formula (VI) can be  
15 used as the monomer (a1) component:



20 wherein:  $R^{VI}$  is hydrogen or methyl;  
 $Z_1$  is O, NH, or  $NR_4$  ( $R_4$  is  $C_{1-4}$ -alkyl); and  
L is



wherein:  $L_1$  and  $L_4$  are each, independently of each other, an alkylene residue having 2 to 6 carbon atoms or a hydroxyalkylene residue having 2 to 6 carbon atoms, and  $L_2$ ,  $L_3$ ,  $L_5$ ,  $L_6$ , and  $L_7$  are alkyl with 1 to 6 carbon atoms, and  $Z^-$  is halide, acetate, or  $CH_3SO_4^-$ .

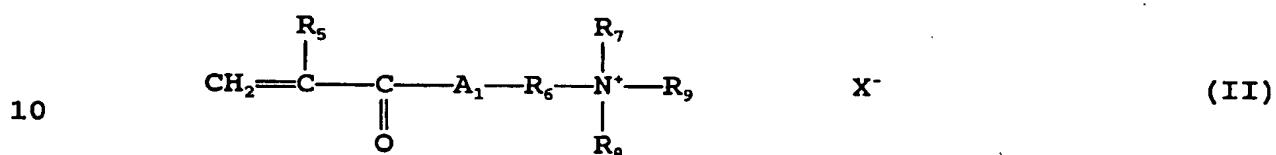
The following might be mentioned as examples of the monomers (a1) of formula (VI): 2-(N,N-dimethylamino)ethyl (meth)acrylate, 3-(N,N-dimethyl-amino)propyl (meth)-acrylate, 4-(N,N-dimethylamino)butyl (meth)acrylate, 2-(N,N-diethylamino)ethyl (meth)acrylate, 2-hydroxy-3-(N,N-dimethylamino)propyl (meth)acrylate, 2-(N,N,N-trimethylammonium)ethyl (meth)acrylate chloride, 3-(N,N,N-trimethylammonium)propyl (meth)acrylate chloride, or 2-hydroxy-3-(N,N,N-trimethylammonium)propyl (meth)acrylate chloride; or the (meth)acrylamides of the above-mentioned compounds, such as, for example, 2-dimethylaminoethyl (meth)acrylamide, 3-dimethylaminopropyl (meth)acrylamide, or 3-trimethylammoniumpropyl (meth)acrylamide chloride.

As monomer (a1) components, one can furthermore use ethylenically unsaturated monomers, that are capable of forming water soluble polymers, such as, for example, vinylpyridine, N-vinylpyrrolidone, styrenesulfonic acid, N-vinylimidazole or diallyldimethylammonium chloride.

Combinations of different water-soluble monomers, listed under (a1), are also possible here. The

(meth)acrylammonium-salts are known in the art and described in, Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 15, pp. 346-376, 3rd. Ed., Wiley Interscience, 1987.

- 5        The amphoteric (a2) monomers, for example, can be monomeric compounds according to formulas (II) or (III):



wherein:  $\text{A}_1$  is O, NH, or  $\text{NR}_4$  wherein  $\text{R}_4$  is alkyl with 1 to 4 carbon atoms;

15         $\text{R}_5$  is hydrogen or methyl;

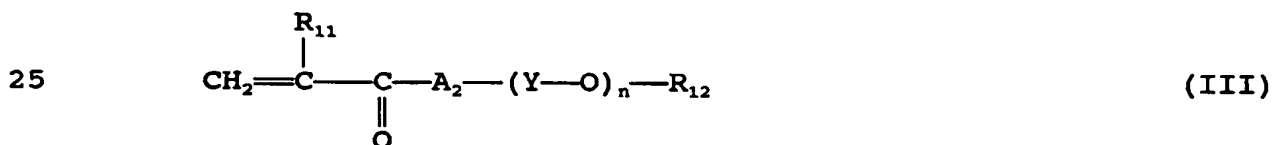
$\text{R}_6$  is alkylene with 1 to 18 carbon atoms;

$\text{R}_7$  and  $\text{R}_8$  each, independently of each other, are alkyl with 1 to 6 carbon atoms;

$\text{R}_9$  is  $\text{C}_{1-32}$ -alkyl,  $\text{C}_{6-32}$ -aryl, and/or  $\text{C}_{7-32}$ -aralkyl;

20        and

$\text{X}^-$  is halide, pseudohalide ( $\text{CN}^-$ ,  $\text{OCN}^-$ , or  $\text{SCN}^-$ ),  $\text{CH}_3\text{SO}_4^-$ , or acetate;



wherein:  $A_2$  is O, NH, or  $NR_{13}$ , wherein  $R_{13}$  is alkyl with 1 to 4 carbon atoms;

$R_{11}$  is hydrogen or methyl;

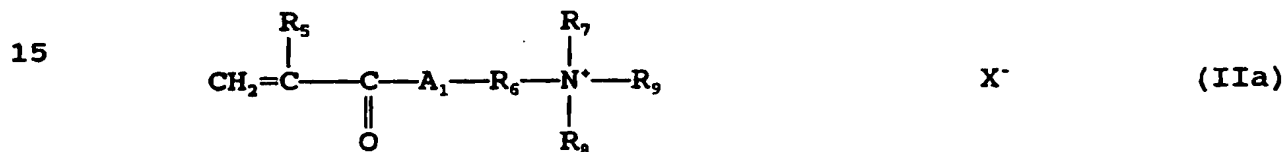
5  $R_{12}$  is hydrogen or alkyl, aryl, and/or aralkyl with 8 to 32 carbon atoms;

$Y$  is alkylene with 2 to 6 carbon atoms; and

$n$  is an integer of 1 to 50.

The amphoteric monomers of formula (II) can be prepared as described in Kirk-Othmer, Encyclopedia of  
 10 Chemical Technology, vol. 1, 3rd. Ed., pp. 330-354 (1978); and vol. 15, pp. 346- to 376 (1981), Wiley Interscience.

The amphoteric monomer (a2) is preferably a compound according to formula IIa:



wherein:  $A^1$  is O, NH, or  $NR_4$  in which  $R_4$  is alkyl with 1 to 4 carbon atoms;

20  $R_5$  is hydrogen or methyl;

$R_6$  is alkylene with 1 to <sup>18</sup> carbon atoms;

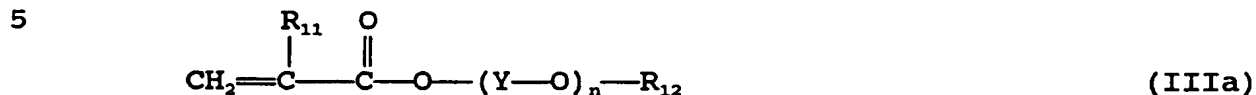
$R_7$  and  $R_8$ , independently of each other, are alkyl with 1 to 6 carbon atoms;

25  $R_9$  is alkyl with 8 to 32 carbon atoms; and



X<sup>-</sup> is halide, pseudohalide, CH<sub>3</sub>SO<sub>4</sub><sup>-</sup>, or  
acetate, in which pseudohalide is CN<sup>-</sup>, OCN<sup>-</sup>, or  
SCN<sup>-</sup>;

or a compound according to formula (IIIa):



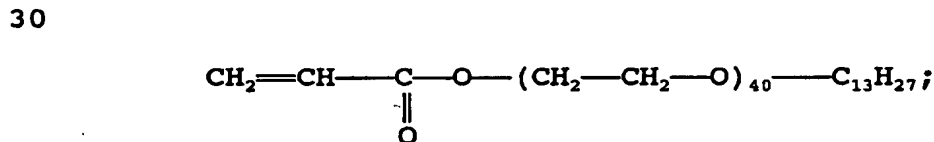
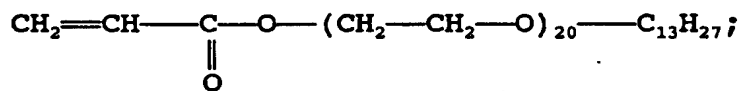
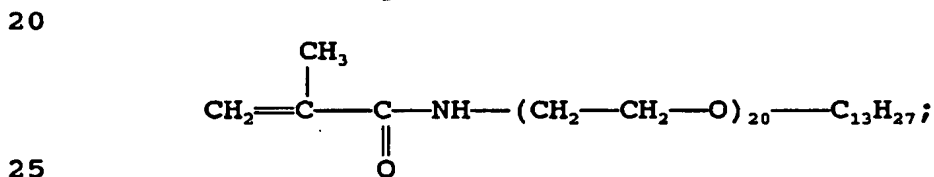
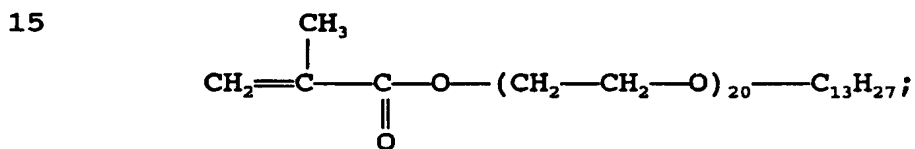
wherein: R<sub>11</sub> is hydrogen or methyl;

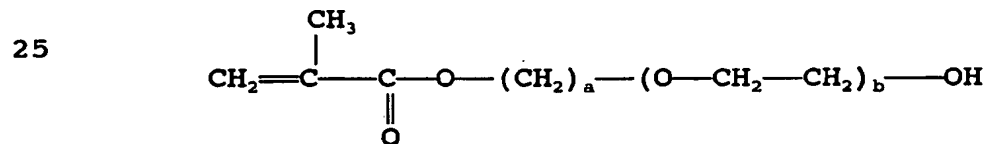
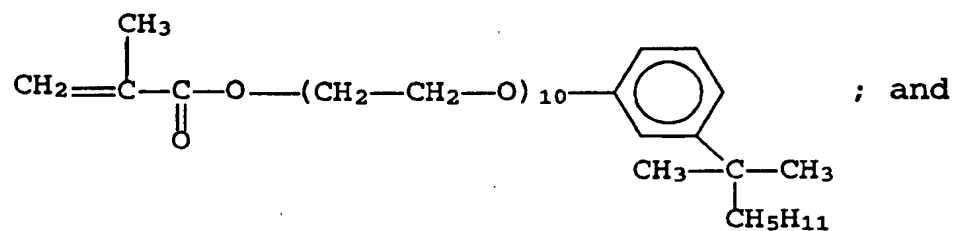
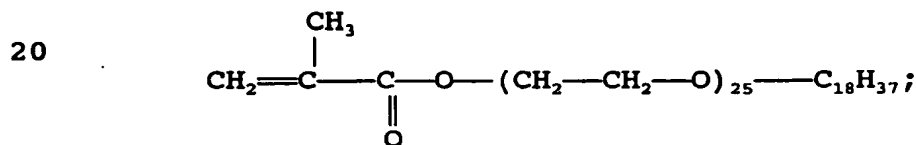
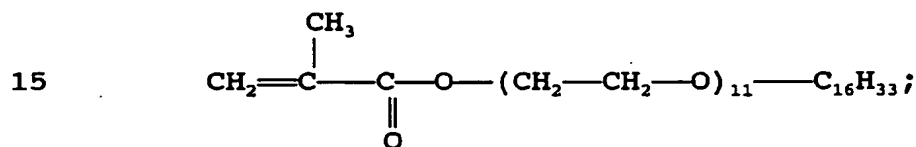
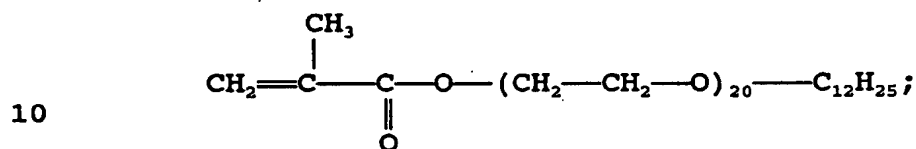
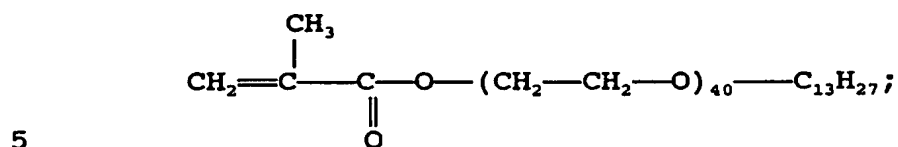
R<sub>12</sub> is hydrogen or alkyl, aryl, and/or aralkyl  
with 8 to 32 carbon atoms;

Y is alkylene with 2 to 6 carbon atoms; and

n is an integer of 1 to 50.

The following might be mentioned as examples of formula  
(III) monomers:

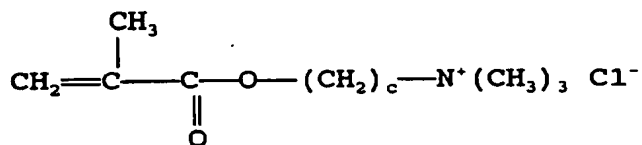




with  $a = 6$  to  $15$  and  $b = 1$  to  $50$ .

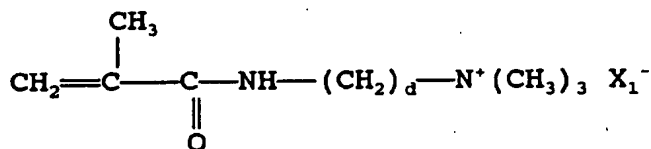
30 Examples of the amphoteric monomers of formula (II) include:

5



with  $c = 6$  to  $18$ ;

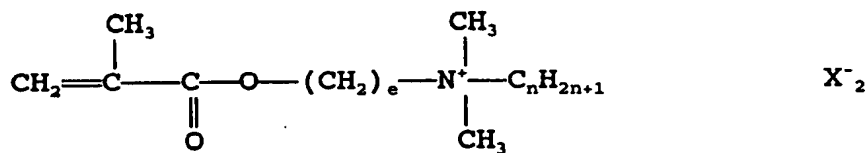
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with  $\text{X}_1^- = \text{Cl}^-$  or  $\text{SO}_4\text{CH}_3^-$  and

$d = 6$  to  $18$ ; or

15



with  $e = 2$  to  $6$ ,  $n = 6$  to  $18$ , and

20

$\text{X}_2^- = \text{Cl}^-$  or  $\text{SO}_4\text{CH}_3^-$

Of course, combinations of the various amphoteric monomers (a2) listed are also possible.

The polymeric dispersion agent differs significantly in terms of the chemical composition and with regard to weight average molecular weight,  $M_w$ , from the water-soluble polymer, consisting of the monomer mixture of monomer (a1) and, optionally monomer (a2), where the polymeric dispersion agent (D) is incompatible with the water-soluble

polymer. The weight average molecular weight,  $M_w$ , of the polymeric dispersion agent is in the range between  $10^3$  to  $5 \times 10^5$  Daltons, preferably between  $10^4$  to  $4 \times 10^5$  Daltons (for the determination of  $M_w$ , see H.F. Mark et al.,  
5 Encyclopedia of Polymer Science and Technology, vol. 10, pp. 1-19, J. Wiley, 1987).

The polymeric dispersion agents (D) contain at least one functional group selected from among ether-, hydroxyl-, carboxyl-, sulfone-, sulfate-ester-, amino-, amido-,  
10 imido-, -tert-amino- and/or quaternary ammonium groups. Examples of polymeric dispersion agent (D) include the following: cellulose derivatives, poly(ethylene glycol), poly(propylene glycol), copolymers from ethylene glycol and propylene glycol, poly(vinyl acetate), poly(vinyl alcohol),  
15 starch and starch derivatives, dextran, polyvinylpyrrolidone, polyvinylpyridine, polyethyleneimine, polyvinylimidazole, polyvinylsuccinimide, poly(vinyl-2-methylsuccinimide), poly(vinyl-1,3-oxazolidone-2), poly(vinyl-2-methylimidazoline), and copolymers, which,  
20 along with combinations from monomeric building blocks of the above-mentioned polymers can, for example, contain the following monomer units: maleic acid, maleic acid anhydride, fumaric acid, itaconic acid, itaconic acid anhydride, methacrylic acid, salts of methacrylic acid or  
25 methacrylamide compounds. As polymeric dispersion agents (D), one preferably uses poly(alkylene ethers), such as,

for example, poly(ethylene glycol), poly(propylene glycol) or poly(butylene-1,4-ether). For the preparation of poly(alkylene ethers), see, for example, Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd. Ed., vol. 18, pp. 616-670, 1982, Wiley Interscience.

As polymeric dispersion agents (D) one particularly prefers to use polyelectrolytes, such as, for example, polymers, containing monomeric building blocks, such as, for example, salts of methacrylic acid as anionic monomer building blocks or derivatives -- quaternized with methylchloride of N,N-dimethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate or N,N-dimethylaminohydroxypropyl (meth)acrylate or N,N-dimethylaminopropyl (meth)acrylamide. Particularly preferred is poly(diallyldimethylammonium chloride) (poly-DADMAC) with a weight average molecular weight,  $M_w$ , between  $5 \times 10^4$  and  $4 \times 10^5$  Daltons as the polymeric dispersion agent. For the preparation of polyelectrolytes, see, for example, Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd. Ed., vol. 18, pp. 495-530, 1982, Wiley Interscience.

Furthermore, one can use low-molecular weight emulsifiers with a molecular weight of  $< 10^3$  Daltons in quantities of 0 to 5% by weight, based on the total weight of the polymer dispersion.

In a first embodiment, the aqueous polymeric dispersion (PD') containing polymer (A) and the polymeric

dispersion agent (D) is made in a single-stage by removing water during the polymerization and possibly by further adding additional polymeric dispersion agent (D). The amount of the monomer mixture of monomer (a1) and, 5 optionally, monomer (a2), that make up the polymer (A) lies between 5 and 80 parts by weight, preferably between 10 and 50 parts by weight, based on 100 parts by weight of the water used as the polymerization medium. When monomer (a1) and, optionally, monomer (a2) are added as an aqueous 10 solution, then the remaining water portion is added to the reaction medium. The quantity of the polymeric dispersion agent (D) suitably lies between 1 and 50 parts by weight, preferably between 2 and 40 parts by weight, and particularly preferably between 5 and 30 parts by weight, 15 per 100 parts by weight of the water used as the reaction medium.

To start the polymerization, for example, one uses radical initiators or high-energy radiation, such as, for example, ultraviolet light. Preference is given, as 20 radical initiators, for example, to 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-aminopropane)dihydrochloride (preferably dissolved in dimethylformamide), preferably 2,2'-azobis[2-(2-imidazolin-2-yl)-propane], potassium persulfate, ammonium persulfate, 25 hydrogen peroxide, possibly in combination with a reducing agent, such as, for example, an amine or a sodium sulfide.

The amount of the initiator is suitably between  $1 \times 10^{-3}$  and 5% by weight, preferably between  $1 \times 10^{-2}$  and 1% by weight, based on the total weight of the monomer mixture of monomer (a1) and, optionally, (a2). The initiator can be added  
5 completely at the start of the polymerization or portionwise or continuously over the entire course of polymerization. Similarly, the monomer mixture of monomer (a1) and, optionally, monomer (a2) can be added completely at the beginning of the polymerization or portionwise or  
10 continuously over the entire course of polymerization.

The polymerization temperature generally is between 0 and 100°C, preferably between 30 and 60°C. Preferably, one polymerizes under an inert gas atmosphere, for example, under a nitrogen atmosphere. The final conversion of  
15 polymerization lies above 98% by weight of the monomer mixture of monomer (a1) and, optionally, monomer (a2) employed, for which one generally requires a polymerization time of between 1 and 8 hours.

During the polymerization, the water content of the  
20 developing polymer dispersion (PD) is preferably reduced by evaporating the water. The water removal can be carried out for example by distilling the water, preferably under reduced pressure or under a vacuum. The distillation apparatuses which may be used here are known, such as, for  
25 example, distillation columns (see also, for example, Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd. Ed. vol.,

7, pp. 849-891, J. Wiley, New York, 1979). Other evaporation units, for example, are convection evaporators or thin-film evaporators (see, for example, Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd. Ed., vol. 9, pp. 472-493, J. Wiley, New York, 1980). Also possible are methods such as membrane diffusion or binding water with organic or inorganic reagents. The water content of the polymeric dispersion (PD') thus made can be reduced to the extent that the viscosity of the resultant polymeric dispersions permits technologically reasonable handling and so long as the dispersion stability so allows.

Preferably, one waits before removing the water until the aqueous solution of the monomers -- containing a part of the polymeric dispersion agent (D) -- has reached reaction temperature, until an inert gas atmosphere prevails over the reaction preparation and until the initiator has been added. In a particularly preferred manner, after adding the initiator, one still waits a certain time, generally between 10 minutes and one hour, before starting to remove the water.

Suitably, 1 to 70 parts by weight, preferably 5 to 60 parts by weight, more preferably 10 to 50 parts by weight, per 100 parts by weight of the total water used as the reaction medium at the outset of the polymerization, of water is removed during the polymerization.



In a second embodiment, the present method further comprises the addition of polymeric dispersion agent (D) in aqueous solution to the polymeric dispersion (PD') formed during stage 1 to make the (PD'') polymeric dispersion. The  
5 addition of the polymeric dispersion agent (D) in aqueous solution to the polymeric dispersion (PD'), formed during the first stage of the process according to the invention, with reduced water content, may take place in static or dynamic mixing units. While the former work by generating  
10 turbulence that develops in the liquid mixture as it flows through the mixers, the turbulence in the dynamic mixers is generated actively (see, for example, Rompps Chemie-Lexikon, 9th Ed. page 2805, Georg Thieme, Stuttgart, New York, 1991). One preferably uses stirrers, such as, for  
15 example, propeller, oblique blade, disk, impeller, crossbar, grill, anchor, screw-spindle or helical ribbon impellers, with special preference given to stirrers that, during the stirring process, generate a small shear ratio [gradient] (see, for example, Rompps Chemielexikon, 9th.  
20 Ed., pp. 3939-3940, Georg Thieme, Stuttgart, New York, 1992).

During the mixing process, the aqueous dispersion of the (PD') polymers is preferably put aside and, thereafter, the polymeric dispersion agent (D) -- that is preferably  
25 employed in aqueous solution -- is added step by step while stirring. In the process, one constantly checks the

viscosity of the mixture. In a particularly preferred embodiment of the invention, the aqueous dispersion of the polymers is heated to between 30 and 90°C, preferably to between 40 and 70°C, to keep the viscosity as low as possible during the mixing process. As a result one gets polymeric dispersions (PD'') with very high active substance concentrations and comparatively very low viscosities. For example, by means of the process according to the present invention, one can double the active substance concentration of a polymeric dispersion (PD''), that represents the sum of the contents of polymer (A) and polymeric dispersion agent (D), for example, with roughly identical viscosity when compared to the viscosity of the polymeric dispersions (PD). In general, (PD'') polymeric dispersions, with an active substance concentration of up to 50% by weight or slightly more, are possible.

In another advantageous embodiment of the present invention, the polymeric dispersion (PD'') can once again have water removed from it in the above-described way, and then the second stage of the process according to the invention can be repeated. As in the case of the addition of the aqueous solution of the dispersion agent (D) in the second stage, there must be no inert gas atmosphere prevailing above the dispersion.

The (PD') or (PD'') polymeric dispersions, made according to the present invention, are characterized by

having a surprisingly low viscosity, judging by the active substance concentration, where the active substance consists of a combination of polymer (A) and dispersion agent (D), and judging by the average molecular weight of the polymer (A). The actual viscosity rises to a very high maximum when the aqueous polymeric dispersions (PD') or (PD'') is diluted with water, and in the process the system becomes clear. The viscosities of the aqueous polymer solution, at 1% by weight polymer content, are on a high level; the (D) poly-DADMAC dispersion agent, which is used on a preferred basis, at the same time acts as active substance, that is to say, as interference substance interceptor in the case of recirculation water and for the support of flocculation, for example, in the course of slurry coagulation. Another advantageous feature of the aqueous polymeric dispersions (PD') or (PD'') according to the present invention is the high shear and standing stability. In that way, the high viscosity of an aqueous solution, with 1% by weight polymer concentration, remains extensively constant even after longer stirring.

The absence of organic solvents ensures safe handling (for example, no flammability) and ecologically unobjectionable use of the polymeric dispersions (PD') or (PD'') according to the present invention, for example, as thickening agents, flocculation aids for electrically charged particles in suspension, as retention agents for

paper-making and/or a soil improvement agents. In isolated or water-poor form, the polymer dispersions according to the present invention can be used as dehydration agents, for example, in the field of hygiene.

5        Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

10

#### EXAMPLES

In the following Examples, the physical data were determined using the following standards:

- Dynamic viscosity  $\eta$  (Pa.s) according to  
DIN 53 018/53 019,
- 15    -        Molecular weight  $M_w$  per gel permeation chromatography  
(see, for example, H.F. Mark et al., Encyclopedia of Polymer Science and Technology, vol. 10, pp. 1-19, J. Wiley, 1987) with standard poly(2-trimethyl-  
ammoniumethyl acrylate chloride),
- 20    -        Stammberge value, STB II (s): Determination of time  
development of Kaolin sedimentation in solutions  
containing flocculation agents after the flocculation  
process: Per liter of pipeline water (20° DH), 20 g  
of kaolin are suspended and the suspension is kept  
25    homogeneous while stirring. Thereafter, 250 ml of  
kaolin suspension are poured into a 250-ml

measurement cylinder and are kept homogeneous while stirring.

The stirring action is interrupted for the purpose of dosing 1 ml of 0.1% aqueous solution of the (PD")  
5 polymeric dispersion (active substance content).

This is followed by another 15 seconds of stirring, whereupon the stirring action is stopped. Thereafter, one takes the time for the decline of the  
10 sedimentation level by 4 cm in the measurement cylinder and that time corresponds to the STB II Stammberge value.

Example 1:

Production and properties of a polymeric dispersion (PD") made according to the 2-stage process:

15 A mixture of 342.5 g of a 40% aqueous poly(diallyldimethylammonium chloride) (poly-DADMAC) solution, 100.0 g of acrylamide, 125.0 g of an 80% aqueous 2-trimethylammoniummethyl acrylate chloride solution, and 432.5 g of water is provided in a reaction vessel with a  
20 nitrogen gas atmosphere and is heated to 62°C while stirring. Subsequently, 0.02 g of 2,2'-azobis[2-(imidazolin-2-yl)-propane] (AIP), dissolved in 0.18 g of water, are added, and a vacuum of 250 mbar is applied to remove the water. After a reaction of 1.5 hour while  
25 stirring, the temperature of the reaction mixture is raised

to 77°C and another 0.2 g of AIP, dissolved in 0.2 g of water, is added while retaining the vacuum. The reaction is completed after another hour of reaction time.

Throughout the entire reaction time of 2.4 hours, 222 g of  
5 water are removed from the reaction mixture at a vacuum of 250 mbar. During the second stage, another 222 g of a 40% aqueous poly-DADMAC-solution is added to the polymeric dispersion (PD') thus formed. The polymeric dispersion (PD''), resulting after the two-stage process, has the  
10 following properties:

Dynamic viscosity:  $\eta_1 = 63,000 \text{ mPa.s}$

Dynamic viscosity of a 1% aqueous solution of the polymer in water (the reference here is the dry content of the polymer (a)):  $\eta_2 = 1,330 \text{ mPa.s}$ .

15 Flock relation value: STB II (S) = 11.3 s

Dry content of (PD'') polymeric dispersion: 42.6%

Molecular weight of the polymer (A), located in the (PD'') polymeric dispersion:  $M_n > 10^6 \text{ Daltons}$ .

Example 2:

Production and properties of a polymeric dispersion (PD'), made according to the single stage process:

A mixture consisting of 275.0 g of a 40% aqueous poly-DADMAC-solution, 75.0 g of acrylamide, 93.8 g of an 80% aqueous 2-trimethylammoniummethyl acrylate chloride solution, and 556.2 g of water is provided in a reaction vessel with a nitrogen gas atmosphere and is heated to 55°C while stirring. Subsequently, 0.015 g of AIP, dissolved in 0.18 g of water, are added, and, after 25 minutes of reaction time, while stirring, a vacuum of 150 mbar is applied to remove the water. After a reaction time of 1.5 hour, the temperature is raised to 65°C and another 0.15 g of AIP, dissolved in 1.35 g of water, are added while maintaining the vacuum. After another 15 minutes of reaction time, the reaction is completed. Throughout the entire reaction time of 1.75 hour, 267 g of water are removed from the reaction mixture at a vacuum of 150 mbar.

The polymeric dispersion (PD'), resulting from the single-stage process, has the following properties:

Dynamic viscosity:  $\eta_1 = 132,000 \text{ mPa.s}$

Dynamic viscosity of a 1% aqueous solution of the polymer in water (the reference here is the dry content of the polymer (A)):  $\eta_2 = 2,200 \text{ mPa.s}$ .

Flocculation value: STB II (s) = 6.8 s

Molecular weight of the polymer (A), located in the polymeric dispersion (PD') =  $M_w > 10^6$  Daltons.

5

This application is based on German Patent Application P 44 01 951.3 filed on January 24, 1994, and published as DE 44 01 951 A1.

10 Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.



CLAIMS

1. A process for making a low-viscosity water-soluble polymeric aqueous dispersion (PD') which has high concentrations of active ingredients, said aqueous dispersion comprising:

(1) a polymer (A), prepared by polymerizing a monomer mixture comprising:

(a1) 80 to 100% by weight, based on the total weight of said monomer mixture, of at least one water-soluble monomer; and, optionally,

(a2) 0 to 20% by weight, based on the total weight of said monomer mixture, of at least one amphoteric monomer,

wherein the sum of the amounts of monomer (a1) and monomer (a2) is 100% by weight and wherein said polymer (A) has a weight average molecular weight,  $M_w$ , of at least  $5 \times 10^5$  Daltons; and

(2) a polymeric dispersion agent (D), which is incompatible with the water-soluble polymer, said polymeric dispersion agent having a weight average molecular weight  $M_w$ , in the range between  $10^3$  to  $5 \times 10^5$  Daltons, and containing at least one functional group selected from the group

consisting of ether-, hydroxyl-, carboxyl-, sulfone-, sulfate-ester-, amino-, amido-, imido-, -tert-amino- and quaternary ammonium groups, wherein said process comprises:

5           (i)     polymerizing said monomer mixture of monomer (a1) and, optionally, monomer (a2) in an aqueous medium wherein said polymerizing is carried out in the presence of said polymeric dispersion agent (D), and  
10           water is removed from said aqueous medium during said polymerization, to obtain said polymeric dispersion (PD').

2.     The process of Claim 1, further comprising:

15           (ii)    adding a portion of an aqueous solution comprising said polymeric dispersion agent (D) to said (PD') polymeric dispersion, to obtain a polymeric dispersion (PD").

20     3.     The process of Claim 2, further comprising:

          (iii)   removing water from said polymeric dispersion (PD"); and

(iv) adding another portion of said aqueous solution comprising said polymeric dispersion agent (D).

5           4. The process of Claim 3, further comprising stepwise repeating steps (iii) and (iv).

5. The process of Claim 1, wherein said polymeric dispersion agent (D) is a polyelectrolyte with a weight  
10 average molecular weight,  $M_w$ , of less than  $5 \times 10^5$  Daltons.

6. The process of Claim 1, wherein said polymeric dispersion agent (D) is a poly(alkylene ether) with alkylene groups having 2 to 6 carbon atoms.

15

7. The process of Claim 1, wherein at least one of said water-soluble monomers (a1) contains at least one ionic group.